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Photoionization of small molecules using synchrotron radiation

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We report here new high-resolution vibrationally resolved studies of photoionization in the molecules CO and CO₂ using synchrotron radiation in the photon-energy range 10-30 eV. The detailed decay dynamics of autoionizing resonances in CO and the origin of symmetry-forbidden vibrational transitions in the \bar{C} state of CO₂⁺ are discussed. These examples illustrate the need for experimental work with both high optical resolution and electron resolution sufficient to resolve the complex resonances in molecules and the vibrational dependence of molecular dynamics.

1. INTRODUCTION

Resonances in molecular photoionization have been a focus of study for understanding molecular dynamics and electronic structure in recent years. Resonances of several types, including Rydberg/valence discrete excitations and continuum shape resonances, temporarily trap electrons within the molecular field.¹ Thus, the interplay of electronic, vibrational, and (ultimately) rotational motion can be explored. The decay of resonant states usually alters the electronic and vibrational populations drastically, revealing non Franck-Condon behavior which is often dominated by electron-electron interactions. In some cases, forbidden vibrational modes of the final ion can be excited solely through correlation effects.²

Because of recent advances in high-resolution and multi-channel detection of electrons, it is now possible to perform angle-resolved experiments on individual vibrational modes of the final ionic state in the photoemission process. This can be done while simultaneously scanning at relatively high optical resolution in the wavelength ranges of these resonances. We discuss here molecular studies on CO and CO₂ to demonstrate these current experimental capabilities and the detailed level at which we can now examine electronic and vibrational motion in the photoionization process.

2. EXPERIMENTAL

Measurements were made with high-resolution 10.2 cm mean-radius hemispherical electron spectrometers equipped with area detectors and placed at $\theta=0^\circ$ and 90° with respect to the major photon polarization axis.³ The experimental chamber is shown schematically in Figure 1, with the

multichannel arrays now used as detectors. We utilized synchrotron radiation from a 2 meter normal incidence monochromator at the SURF-II storage ring at the National Bureau of Standards (NBS). This monochromator disperses radiation in the 10-30 eV range with about 70% linear polarization.⁴ The light polarization (P) was determined to be constant over the range of these experiments using a triple-reflection analyzer.⁵ Since the polarization measured with this device is sensitive to mirror coatings and thus optical reflectivities, we calibrated the absolute polarization with He I_s ionization, which has a known β of 2.0. The resolution of the monochromatic light beam was 0.65(5) Å, which corresponds to about 16 meV at 17.5 eV. For these studies, the electron spectrometers were operated at 5 eV pass energy, and in some cases 2 eV pass energy for the CO₂ work. The widths of the peaks in the photoelectron spectra (full width at half maximum, FWHM) were typically 45 meV for the CO₂ study (at 2 eV pass energy) and 58 meV for the CO study (at 5 eV pass energy).

With this apparatus, we extract branching ratios (BR_v) and angular distribution asymmetry parameters (β_v) as a function of photon energy for an individual vibrational level, v , from the relation:

$$(dN_v/d\Omega) = N_v [1 + (\beta_v/4)(3P\cos 2\theta + 1)]. \quad (1)$$

Here $dN_v/d\Omega$ is the number of electrons ejected per unit light flux per unit solid angle, and is proportional to the differential cross section. In practice, we determine BR_v for a particular vibrational level, which is N_v divided by the sum over N_v for an electronic transition.

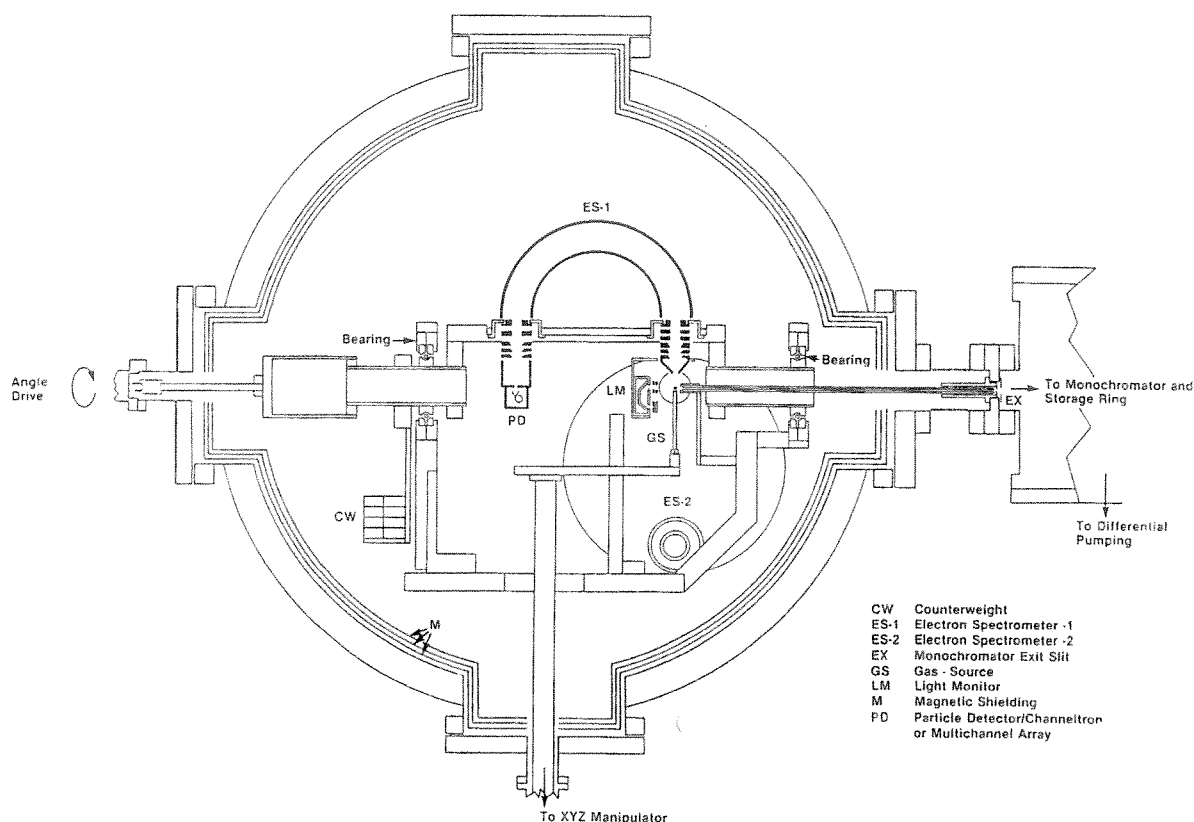


Figure 1: Schematic view of the photoelectron spectrometer system and chamber. ES1 is rotatable through 90°, and ES2 is fixed at 0°, along the major polarization axis of the light.

3. AUTOIONIZATION IN CO

In the photon-energy range of 16-19 eV, the CO molecule exhibits a large number of Rydberg autoionization resonances which appear in the partial photoionization cross sections for the \tilde{X} and A states.⁶⁻⁸ Theory indicates that some of these resonances appear to be complex in nature. This is due to the overlap of the host series leading to the high vibrational thresholds of the A ($^2\Pi$) state with the interloper Rydberg members of series leading to the B ($^2\Sigma^+$) thresholds.⁸⁻⁹ Theoretical effort has centered on the 17-17.5 eV range,⁹ where 2-step Multi-channel Quantum Defect Theory (MQDT) has had some success in reproducing vibrationally unresolved cross sections.⁸ This method requires *ab initio* calculation of the quantum defects and transition amplitudes, which makes CO an especially difficult but important diatomic molecule for study.

In addition, the large number of available vibrational levels (both of the \tilde{X} and A states) makes CO a strong test of the theoretical description of the decay dynamics into electronic and vibrational levels. In MQDT, the vibrational channels are currently introduced by a Condon factorization of the transition

moments and interchannel interactions. The important vibrational levels of the \tilde{X} , A, and B states have been included in this manner in the most recent calculation.⁹

To complement this theoretical work, we have measured the branching ratios and β 's for the $v=0,1$, and 2 vibrational levels of the \tilde{X} state in the energy range 16.8-18.6 eV.¹⁰ We show in Figure 2 the branching ratios for the $v=0$ and $v=1$ levels of the \tilde{X} state, with an energy mesh of 4 meV in the range 17-17.5 eV. The branching ratios are defined here as the cross-section ratio of one vibrational level relative to the sum of the $v=0,1$, and 2 levels of the \tilde{X} state. In most cases, the higher vibrational levels ($v=1,2$) of the \tilde{X} state are enhanced, with a relative loss of intensity in the $v=0$ level. This redistribution of intensity from strong to weak vibrational levels is dramatic and characteristic of autoionization in molecules. In addition, the β results for the $v=0$ level are shown in Figure 3. The β parameter undergoes oscillations with a variety of lineshapes exhibited, which are not generally reproduced by theory.⁹

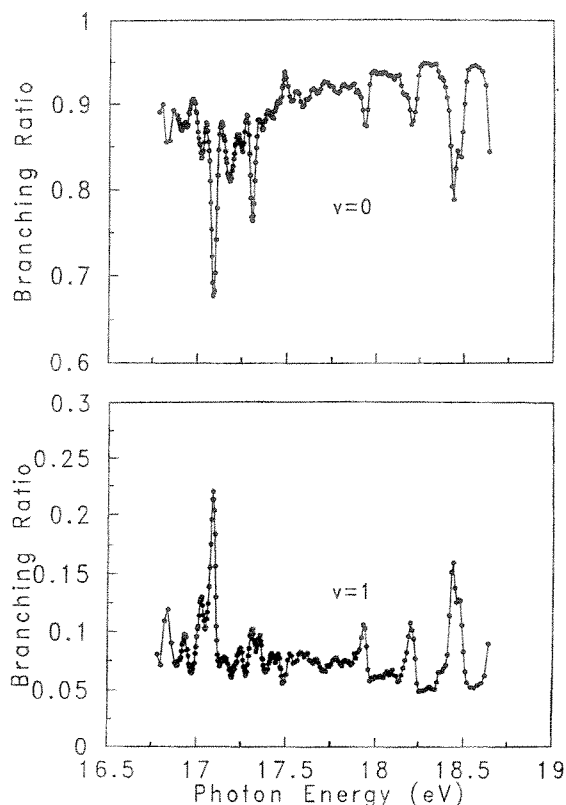


Figure 2: The branching ratios BR_0 ($v=0$) and BR_1 ($v=1$) for the \tilde{X} state of CO^+ between 16.8 and 18.6 eV photon energy.

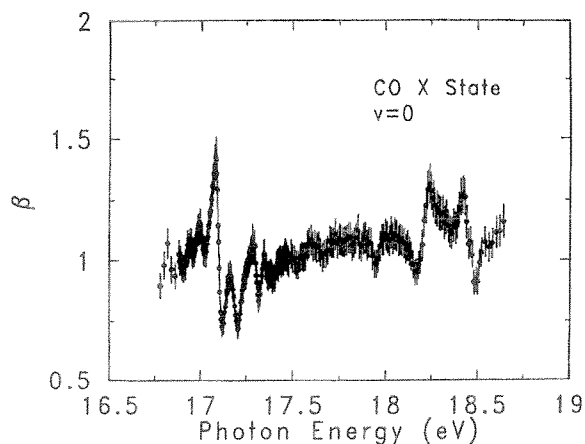


Figure 3: β for the $v=0$ level of the \tilde{X} state of CO^+ between 16.8 and 18.6 eV.

We emphasize, therefore, that there is a continuing need for experimental data of the quality shown here: with both high optical resolution and electron resolution to resolve vibrational levels. The interplay of experiments of this type with theory (MQDT) is especially important to develop a proper description of the detailed decay dynamics for autoionization in CO and other small molecules.

4. VIBRONIC COUPLING IN CO_2^+

In the photoemission of small molecules, a symmetry forbidden transition to a particular vibrational level of the residual ion can sometimes occur. The intensity of such a state can not be explained within the Franck-Condon or adiabatic approximation. An example of this phenomenon occurs in the photoelectron spectrum of the 4th electronic state of CO_2^+ ($\tilde{C}, 2\Sigma_g^+$), shown in Figure 4. The vibrational peaks assigned as (1,0,1) and (0,1,0) are forbidden for transitions from the fundamental neutral state. However, their intensity can be explained by considering how the vibrational motion of the molecules couples different electronic states in the final ion, an interaction called vibronic coupling.²

We have taken photoelectron spectra of the \tilde{C} state in the photon-energy range of 20-28.5 eV to characterize the role of vibronic coupling, particularly for the (1,0,1) vibrational level.¹¹ We emphasize here the β results for the $\tilde{C}(0,0,0)$ and $\tilde{C}(1,0,1)$ transitions with binding energies of 19.387 and 19.747 eV, respectively.¹² We note that the assignment of the second peak as (1,0,1) is uncertain; (0,0,1) is another possible assignment.¹²⁻¹³ Previous work with resonance lamps (He I) indicates significant differences between $\beta(1,0,1)$ and $\beta(0,0,0)$.¹³ Our β results are shown in Figure 5, demonstrating that this difference persists in the first 8 eV above threshold. Our β results for the symmetry-allowed $\tilde{C}(1,0,0)$ transition are, in contrast, generally quite similar to those for the $\tilde{C}(0,0,0)$ level.

This comparison indicates the sensitivity of β to the subtle effects of vibronic coupling. Domcke² has proposed that the kinetic-energy dependence for the β curve of a symmetry-forbidden transition may mimic the β curve of the electronic state to which it couples. For the peak at 19.747 eV, the electronic symmetry $\tilde{C}(2\Sigma_g^+)$ and the vibrational symmetries ($\nu_1=\Sigma_g$, $\nu_3=\Sigma_u$) couple to yield a combined total symmetry of Σ_u . If this forbidden state derives intensity from the intense ν_1 modes of the other electronic states, then only the ν_1 (Σ_g) modes of the $\tilde{B}(2\Sigma_u^+)$ state give the same total symmetry of Σ_u .

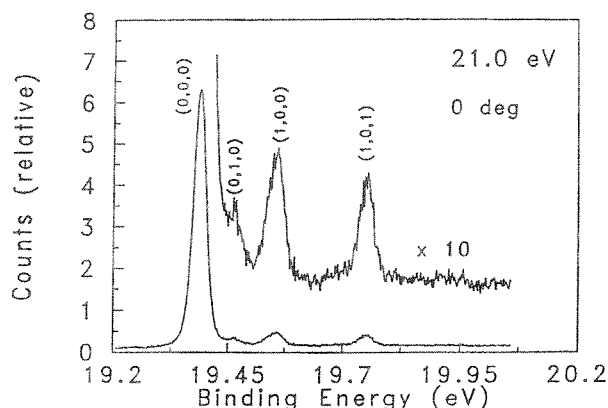


Figure 4: Photoelectron spectrum of the $\bar{C}(^2\Sigma_g^+)$ state of CO_2^+ taken at 2 eV pass energy.

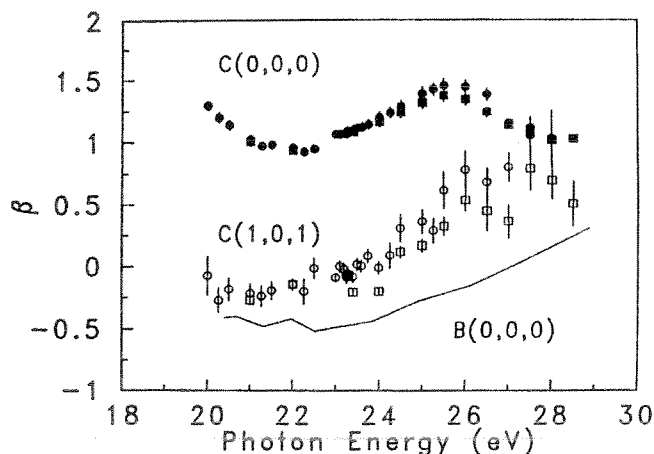


Figure 5: β results for the $\bar{C}(0,0,0)$ (solid symbols) and $\bar{C}(1,0,1)$ (open symbols) vibrational levels of CO_2^+ . Results for both 5 eV (circles) and 2 eV (squares) pass energy are shown. The solid line is drawn through experimental results¹⁴ for the $\bar{B}(0,0,0)$ state as a function of kinetic energy.

Therefore, we show in Figure 5 the experimental β results¹⁴ for the $(0,0,0)$ level of the \bar{B} state of CO_2^+ , plotted as a function of kinetic energy. The similarity to the β for the $\bar{C}(1,0,1)$ level supports the role of vibronic coupling with the $\bar{B}(^2\Sigma_u^+)$ state. Additional effects like molecular geometry, interchannel coupling, and shape resonances will also contribute to

the shape of the β curves, perhaps explaining the shift in absolute magnitude between curves for the forbidden and \bar{B} state transitions.

In summary, we have shown that in this case it seems possible to identify the origin of the vibronic coupling from the β dependence of the forbidden peak. Theoretical work is needed to confirm the peak assignment and this interpretation.

5. ACKNOWLEDGEMENTS

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